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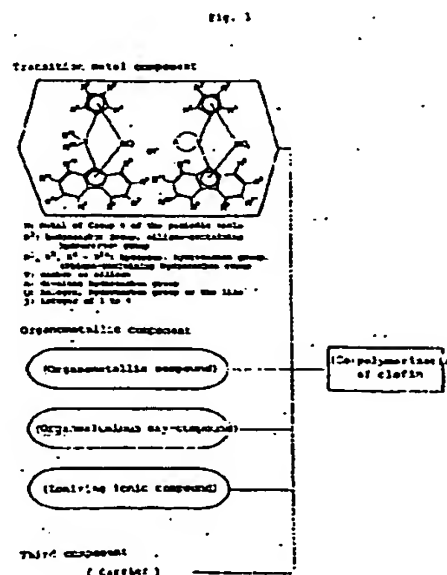
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(54) **METALLOCENE COMPOUND, PROCESS FOR PRODUCING METALLOCENE COMPOUND, OLEFIN POLYMERIZATION CATALYST, PROCESS FOR PRODUCING POLYOLEFIN, AND POLYOLEFIN**

(57) The metallocene compound according to the invention and the olefin polymerization catalyst containing the compound are intended to produce a catalyst capable of preparing an isotactic polymer with a high polymerization activity. The metallocene compound contains a substituted cyclopentadienyl group and a (substituted) fluorenyl group and has a structure wherein these groups are bridged by a hydrocarbon group or the like. The process for preparing a metallocene compound according to the invention is intended to selectively prepare a specific metallocene compound so as not to produce an isomer, and in this process an intermediate product is synthesized by a specific method. The process for preparing a polyolefin according to the invention is intended to prepare a polyolefin having excellent impact resistance and transparency, and this process comprises homopolymerizing an  $\alpha$ -olefin of 3 to 8 carbon atoms or copolymerizing an olefin of 3 to 8 carbon atoms and another  $\alpha$ -olefin in the presence of

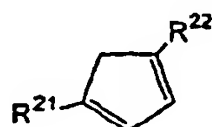
an olefin polymerization catalyst containing the above-mentioned metallocene compound.



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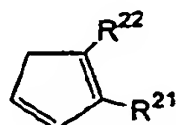
wherein  $R^{21}$ ,  $R^{22}$ ,  $R^{13}$ ,  $R^{14}$ , Y and A have the same meanings as those of  $R^{21}$ ,  $R^{22}$ ,  $R^{13}$ ,  $R^{14}$ , Y and A in the formula (1b) or (2b), respectively.

[0015] In the present invention, furthermore, it is preferable that cyclopentadiene represented by the following formula (19b) is selectively prepared so as not to include an isomeric compound represented by the following formula (20b) and the resulting cyclopentadiene is used as a material to selectively prepare the precursor compound represented by the formula (13b) or (14b);



... (19b)

wherein  $R^{21}$  and  $R^{22}$  have the same meanings as those of  $R^{21}$  and  $R^{22}$  in the formula (1b) or (2b), respectively; and the cyclopentadienyl group may be another isomer different in only the position of a double bond in the cyclopentadienyl ring or a mixture thereof;



: ... (20b)

wherein  $R^{21}$  and  $R^{22}$  have the same meanings as those of  $R^{21}$  and  $R^{22}$  in the formula (1b) or (2b), respectively; and the cyclopentadienyl group may be another isomer different in only the position of a double bond in the cyclopentadienyl ring or a mixture thereof.

[0016] The olefin polymerization catalyst according to the invention comprises any one of the above-mentioned metallocene compounds.

[0017] The olefin polymerization catalyst of the invention may be an olefin polymerization catalyst comprising:

- (A) any one of the above-mentioned metallocene compounds, and
- (B) at least one compound selected from:

- (B-1) an organometallic compound,
- (B-2) an organoaluminum oxy-compound, and
- (B-3) a compound which reacts with the metallocene compound (A) to form an ion pair.

[0018] The olefin polymerization catalyst of the invention may be an olefin polymerization catalyst comprising the above-mentioned olefin polymerization catalyst and (C) a particle carrier.

[0019] The process for preparing a polyolefin according to the invention comprises polymerizing or copolymerizing an olefin in the presence of any one of the above-mentioned olefin polymerization catalysts.

[0020] In the present invention, it is preferable that the metallocene compound (A) is a metallocene compound represented by the formula (1) or (2) and at least 2 kinds of olefins are copolymerized. It is also preferable that the metallocene compound (A) is a metallocene compound represented by the formula (1a) or (2a) and a single olefin is polymerized.

[0021] The polyolefin according to the invention comprises recurring units ( $U_1$ ) derived from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms in amounts of 50 to 100 % by mol and recurring units ( $U_2$ ) other than the recurring units ( $U_1$ ), said recurring units ( $U_2$ ) being derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms in amounts of 50 to 0 % by mol, and has the following properties:

- (i) the proportion of 2,1-Insertion and the proportion of 1,3-Insertion are each not more than 0.2 %,
- (ii) the molecular weight distribution (Mw/Mn) as determined by gel permeation chromatography is in the range of 1 to 3, and
- (iii) the quantity of a decane-soluble component is not more than 2 % by weight.

[0022] The polyolefin preferably comprises recurring units derived from propylene in amounts of 50 to 99.5 % by mol and recurring units derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms other than propylene in amounts of 50 to 0.5 % by mol.

[0023] Another embodiment of the polyolefin of the invention is a homopolymer of one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms and has the following properties:

- (i) the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 85 %,
- (ii) the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %,
- (iii) the MFR is in the range of 0.01 to 1000 g/10 min,
- (iv) the molecular weight distribution (Mw/Mn) as determined by gel permeation chromatography is in the range of 1 to 3,
- (v) the quantity of a decane-soluble component is not more than 2 % by weight, and
- (vi) the melting point (Tm) as measured by a differential scanning calorimeter is not lower than 140°C.

[0024] The polyolefin is preferably a homopolymer of propylene.

[0025] A further embodiment of the polyolefin of the invention is a polyolefin comprising recurring units ( $U_1$ ) derived from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms in amounts of 95 to 99.5 % by mol and recurring units ( $U_2$ ) other than the recurring units ( $U_1$ ), said recurring units ( $U_2$ ) being derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms, in amounts of 5 to 0.05 % by mol, and has the following properties:

- (i) the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 80 %,
- (ii) the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %,
- (iii) the MFR is in the range of 0.01 to 1000 g/10 min,
- (iv) the molecular weight distribution (Mw/Mn) as determined by gel permeation chromatography is in the range of 1 to 3,
- (v) the quantity of a decane-soluble component is not more than 2 % by weight, and
- (vi) the melting point (Tm) as measured by a differential scanning calorimeter is not higher than 145°C.

[0026] The polyolefin preferably comprises recurring units derived from propylene in amounts of 95 to 99.5 % by mol and recurring units derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms other than propylene in amounts of 5 to 0.5 % by mol.

#### BRIEF DESCRIPTION OF THE DRAWING

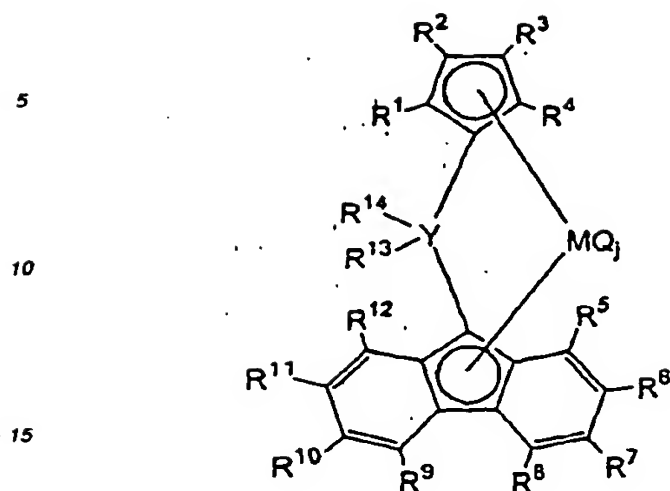
[0027] Fig. 1 is a view to explain an embodiment of a process for preparing the olefin polymerization catalyst according to the present invention.

#### BEST MODE FOR CARRYING OUT THE INVENTION

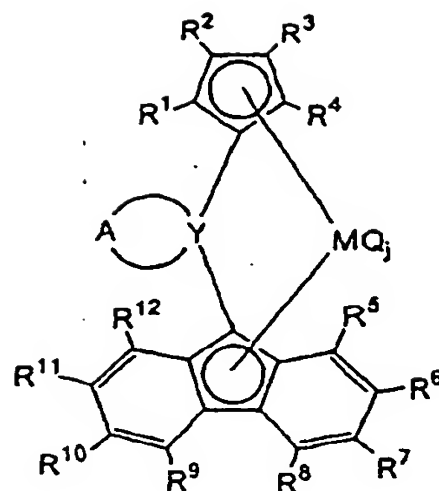
[0028] The metallocene compound, the process for preparing the metallocene compound, the olefin polymerization catalyst, the process for preparing a polyolefin, and the polyolefin according to the invention are described in detail hereinafter.

#### Metallocene compound

[0029] The metallocene compound according to the invention is represented by the following formula (1) or (2).



... (1)



... (2)

[0030] In the formula (1) or (2),  $R^3$  is selected from a hydrocarbon group and a silicon-containing hydrocarbon group.

[0031] The hydrocarbon group preferably is, for example, an alkyl group of 1 to 20 carbon atoms, an arylalkyl group of 7 to 20 carbon atoms, an aryl group of 6 to 20 carbon atoms or an alkylaryl group of 7 to 20 carbon atoms.  $R^3$  may be a cyclic hydrocarbon group containing a heteroatom (e.g., sulfur or oxygen), such as thienyl or furyl.

[0032] Specific examples of such groups include methyl, ethyl, n-propyl, isopropyl, 2-methylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1,1-diethylpropyl, 1-ethyl-1-methylpropyl, 1,1,2,2-tetramethylpropyl, sec-butyl, tert-butyl, 1,1-dimethylbutyl, 1,1,3-trimethylbutyl, neopentyl, cyclohexylmethyl, cyclohexyl, 1-methyl-1-cyclohexyl, 1-adamantyl, 2-adamantyl, 2-methyl-2-adamantyl, menthyl, norbornyl, benzyl, 2-phenylethyl, 1-tetrahydronaphthyl, 1-methyl-1-tetrahydronaphthyl, phenyl, naphthyl and tolyl.

[0033] The silicon-containing hydrocarbon group is preferably an alkylsilyl or arylsilyl group having 1 to 4 silicon atoms and 3 to 20 carbon atoms.

[0034] Specific examples of such groups include trimethylsilyl, tert-butyldimethylsilyl and triphenylsilyl.

[0035]  $R^3$  is preferably a sterically bulky substituent group, more preferably a substituent group of 4 or more carbon atoms.

[0036] In the formula (1) or (2),  $R^1$ ,  $R^2$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $R^{14}$  may be the same or different and are each selected from a hydrogen atom, a hydrocarbon group and a silicon-containing hydrocarbon group. Preferred examples of the hydrocarbon groups and the silicon-containing hydrocarbon groups include the same ones as described above.

[0037] The neighboring substituent groups of  $R^1$  to  $R^4$  on the cyclopentadienyl ring may be bonded to form a ring. Examples of such substituted cyclopentadienyl groups include indenyl, 2-methylindenyl, tetrahydroindenyl, 2-methyl-tetrahydroindenyl and 2,4,4-trimethyltetrahydroindenyl.

[0038] The neighboring substituent groups of  $R^5$  to  $R^{12}$  on the fluorene ring may be bonded to form a ring. Examples of such substituted fluorenyl groups include benzofluorenyl, dibenzofluorenyl, octahydrodibenzofluorenyl and octamethyloctahydrodibenzofluorenyl.

[0039] The substituent groups of  $R^5$  to  $R^{12}$  on the fluorene ring are preferred to be bilaterally symmetric from the viewpoint of ease of synthesis. That is,  $R^5$  and  $R^{12}$ ,  $R^6$  and  $R^{11}$ ,  $R^7$  and  $R^{10}$ , and  $R^8$  and  $R^9$  are preferred to be the same groups, and unsubstituted fluorene, 3,6-di-substituted fluorene, 2,7-di-substituted fluorene or 2,3,6,7-tetra-substituted fluorene is more preferred. The 3-position, 6-position, 2-position and 7-position of the fluorene ring correspond to  $R^7$ ,  $R^{10}$ ,  $R^6$  and  $R^{11}$ , respectively.

[0040] In the formula (1) or (2), Y is a carbon atom or a silicon atom.

[0041] In the metallocene compound represented by the formula (1),  $R^{13}$  and  $R^{14}$  are bonded to Y and become a bridge part to form a substituted methylene group or a substituted silylene group. Preferred examples thereof include methylene, dimethylmethylene, diethylmethylene, diisopropylmethylene, methyl-tert-butylmethylene, di-tert-butylmethylene, dicyclohexylmethylene, methylcyclohexylmethylene, methylphenylmethylene, diphenylmethylene, methyl-naphthylmethylene, dinaphthylmethylene, dimethylsilylene, diisopropylsilylene, methyl-tert-butylsilylene, dicyclohexylsilylene, methylcyclohexylsilylene, methylphenylsilylene, diphenylsilylene, methyl-naphthylsilylene and dinaphthylsilylene.

[0042] In the metallocene compound represented by the formula (1), a substituent group selected from  $R^1$ ,  $R^4$ ,  $R^5$

by adding hydrogen in amount of about 0.01 to 100 NL based on 1 kg of the olefin.

[0197] In the present invention, as olefins used in the polymerization reaction preferable are those of 2 to 20 carbon atoms, particularly  $\alpha$ -olefins of 2 to 10 carbon atoms. Example of the olefins include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, vinylcyclohexane and styrene.

[0198] Further examples include dienes of 4 to 20 carbon atoms such as butadiene, 1,4-pentadiene, 1,5-hexadiene and 1,4-hexadiene, cycloolefins such as dicyclopentadiene, norbornene, methylnorbornene, tetracyclododecene and methyltetracyclododecene and silicon-containing olefins such as allyltrimethylsilane and vinyltrimethylsilane.

[0199] Of the olefin polymerization catalysts according to the invention, the catalyst containing the metallocene compound represented by the formula (1) or (2) is favorably used for copolymerization of at least 2 kinds of olefins.

[0200] At least one of the olefins used is preferably an  $\alpha$ -olefin of 4 or less carbon atoms.

[0201] The copolymerization of two or more olefins using the olefin polymerization catalyst of the invention has advantages such as high polymerization activity and good copolymerizability and is characterized in that a copolymer of desired properties can be obtained.

[0202] An example of the copolymer obtained from two or more olefins is a copolymer comprising recurring units ( $U_1$ ) derived from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms in amounts of 50 to 99.9 % by mol and recurring units ( $U_2$ ) other than the recurring units ( $U_1$ ), said recurring units ( $U_2$ ) being derived from at least one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms, in amounts of 50 to 0.1 % by mol.

[0203] Examples of the  $\alpha$ -olefins of 3 to 8 carbon atoms include propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene and 1-octene. Examples of the  $\alpha$ -olefins of 2 to 20 carbon atoms include the same ones as described above.

[0204] Such a copolymer is, for example, a copolymer comprising propylene units in amounts of 50 to 99.5 % by mol and units of an  $\alpha$ -olefin of 2 to 20 carbon atoms other than propylene in amounts of 50 to 0.5 % by mol.

[0205] The random copolymer comprising propylene units in amounts of 95 to 99.5 % by mol and units of an  $\alpha$ -olefin of 2 to 20 carbon atoms other than propylene in amounts of 5 to 0.5 % by mol preferably has the following properties: the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 80 %, preferably not less than 85 %; the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %; the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min; the molecular weight distribution ( $M_w/M_n$ ) as calculated from molecular weights ( $M_w$ : weight-average molecular weight,  $M_n$ : number-average molecular weight) measured by gel permeation chromatography (GPC) is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3; and the quantity of a decane-soluble component (after the polymer is treated with n-decane at 150°C for 2 hours and cooled to room temperature, the amount (weight %) of the polymer dissolved in the n-decane is measured) is not more than 2 % by weight, preferably not more than 1 % by weight.

[0206] Of the olefin polymerization catalysts according to the invention, the catalyst containing the metallocene compound represented by the formula (1a) or (2a) is favorably used for homopolymerization of an olefin.

[0207] The homopolymerization of an  $\alpha$ -olefin of 3 or more carbon atoms using the olefin polymerization catalyst of the invention is characterized in that an olefin polymer having high stereoregularity can be obtained and the polymer usually has high isotacticity.

[0208] The homopolymer of an  $\alpha$ -olefin of 3 or more carbon atoms, particularly polypropylene, preferably has the following properties: the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 85 %, preferably not less than 90 %, more preferably not less than 95 %; the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %, more preferably not more than 0.05 %; the melting point ( $T_m$ ) as measured by differential scanning calorimetry (DSC) is not lower than 140°C, preferably not lower than 150°C, more preferably not lower than 153°C; the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min; the molecular weight distribution ( $M_w/M_n$ ) as calculated from molecular weights measured by GPC is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3; and the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by weight, more preferably not more than 0.5 % by weight.

[0209] Of the olefin polymerization catalysts according to the invention, the catalyst containing the metallocene compound represented by the formula (1b) or (2b) is favorably used for homopolymerization of an olefin or copolymerization of at least two kinds of olefins.

[0210] Of the polymers obtained by the use of such a catalyst, a homopolymer of an  $\alpha$ -olefin of 3 to 8 carbon atoms, particularly polypropylene, preferably has the following properties: the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 85 %, preferably not less than 90 %, more preferably not less than 95 %; the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %, more preferably not more than 0.05 %; the melting point ( $T_m$ ) as measured by DSC is not lower than 140°C,

preferably not lower than 150°C, more preferably not lower than 153°C; the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min; the molecular weight distribution (Mw/Mn) as calculated from molecular weights measured by GPC is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3; and the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by weight, more preferably not more than 0.5 % by weight.

[0211] An example of the copolymer obtained from two or more olefins using the catalyst containing the metallocene compound represented by the formula (1b) or (2b) is a copolymer comprising recurring units ( $U_1$ ) derived from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms in amounts of 50 to 99.9 % by mol and recurring units ( $U_2$ ) other than the recurring units ( $U_1$ ), said recurring units ( $U_2$ ) being derived from at least one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms, in amounts of 50 to 0.1 % by mol.

[0212] Such a copolymer is, for example, a copolymer comprising propylene units in amounts of 50 to 99.5 % by mol and units of an  $\alpha$ -olefin other than propylene in amounts of 50 to 0.5 % by mol.

[0213] The copolymer comprising propylene units in amounts of 95 to 99.5 % by mol and units of an  $\alpha$ -olefin of 2 to 20 carbon atoms other than propylene in amounts of 5 to 0.5 % by mol preferably has the following properties: the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 80 %, preferably not less than 85 %; the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %; the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min; the molecular weight distribution (Mw/Mn) as calculated from molecular weights measured by GPC is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3; and the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by weight.

#### Polyolefin

[0214] The polyolefin according to the invention is a polyolefin comprising recurring units ( $U_1$ ) derived from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms in amounts of 50 to 100 % by mol, preferably 65 to 100 % by mol, more preferably 80 to 100 % by mol, and recurring units ( $U_2$ ) other than the recurring units ( $U_1$ ), said recurring units ( $U_2$ ) being derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms, in amounts of 50 to 0 % by mol, preferably 35 to 0 % by mol, more preferably 20 to 0 % by mol.

[0215] Examples of the  $\alpha$ -olefins of 3 to 8 carbon atoms and the  $\alpha$ -olefins of 2 to 20 carbon atoms include the same ones as previously described.

[0216] This polyolefin satisfies the following requisites (i) to (iii):

(i) the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %,

(ii) the molecular weight distribution (Mw/Mn) as determined by (GPC) is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3, and

(iii) the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by weight.

[0217] The polyolefin preferably comprises recurring units derived from propylene in amounts of 50 to 99.5 % by mol, preferably 65 to 99.5 % by mol, more preferably 80 to 99.5 % by mol, and recurring units derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms other than propylene in amounts of 50 to 0.5 % by mol, preferably 35 to 0.5 % by mol, more preferably 20 to 0.5 % by mol.

[0218] Such a polyolefin of the invention has excellent elastic modulus, impact resistance and transparency.

[0219] Another embodiment of the polyolefin of the invention is a homopolymer of one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms.

[0220] Examples of the  $\alpha$ -olefins of 3 to 8 carbon atoms include the same ones as previously described.

[0221] This polyolefin satisfies the following requisites (i) to (vi):

(i) the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 85 %, preferably not less than 90 %, more preferably not less than 95 %,

(ii) the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %, more preferably not more than 0.05 %,

(iii) the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min, more preferably 0.02 to 400 g/10 min,

(iv) the molecular weight distribution (Mw/Mn) as determined by GPC is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3,

(v) the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by

lution of n-butyllithium was dropwise added in a nitrogen atmosphere with ice cooling. The mixture was reacted overnight while allowing the temperature of the mixture to naturally rise to room temperature, to obtain a red solution. The solution was cooled to -78°C again, and 0.60 g (1.60 mmol) of zirconium tetrachloride (THF) 2-complex was added in a nitrogen atmosphere. The mixture was reacted overnight while allowing the temperature of the mixture to naturally rise to room temperature similarly to the above. The resulting red suspension was subjected to seltite filtration to remove a white solid. Then, the red filtrate was concentrated and dried to obtain a crude red solid. The solid was recrystallized from 5 ml of diethyl ether to obtain 116 mg of a red solid. The analyzed values are given below.

<sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS): δ 7.98 (2H), 7.45 (d, 2H), 6.05 (t, 1H), 5.48 (t, 1H), 5.37 (t, 1H), 3.48 (m, 4H), 2.68 (m, 4H), 2.06-0.99 (36H)  
FD-MS: m/z = 732, 734, 736 (M<sup>+</sup>)

#### Example 25

##### Bulk copolymerization of propylene and ethylene using dimethylmethylen(3-tert-butyl-5-methylcyclopentadienyl) fluorenylzirconium dichloride

[0381] In a 50 ml two-necked flask thoroughly purged with nitrogen, 0.72 mmol (in terms of aluminum) of silica-supported methylaluminoxane was suspended in 20 ml of heptane. To the suspension, a toluene solution of 0.65 mg (1.3 μmol) of the reddish orange solid obtained in Example 1 was added, then triisobutylaluminum (0.33 mmol) and triethylaluminum (1.0 mmol) were added as alkylaluminum, and they were stirred for 30 minutes to give a catalyst suspension.

[0382] A 2000 ml autoclave thoroughly purged with nitrogen was charged with 400 g of propylene and 2NL of an ethylene gas, and the catalyst suspension was added to perform polymerization at 60°C for 60 minutes under a pressure of 3.0 to 3.5 MPa. Thereafter, methanol was added to terminate the polymerization, and propylene was purged of, to obtain a polymer. The polymer was dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 127 g. This polymer had Tm of 128°C, MFR of 5.5 g/10 min and a decane-soluble component quantity of 0.2 % by weight.

#### Example 26

##### Bulk copolymerization of propylene and ethylene using dimethylmethylen(3-tert-butyl-5-methylcyclopentadienyl) fluorenylzirconium dichloride

[0383] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 25, except that the charge of ethylene was changed to 3 NL. The quantity of the polymer obtained was 146 g. This polymer had Tm of 124°C, MFR of 5.5 g/10 min and a decane-soluble component quantity of 0.3 % by weight.

#### Example 27

##### Bulk copolymerization of propylene and ethylene using dimethylmethylen(3-tert-butyl-5-methylcyclopentadienyl) fluorenylzirconium dichloride

[0384] Polymerization was carried out in the same manner as in Example 25, except that the silica-supported methylaluminoxane was used in an amount of 0.52 mmol in terms of aluminum, and only the triethylaluminum (1.3 mmol) was used as alkylaluminum. The quantity of the polymer obtained was 79 g. This polymer had Tm of 124°C, MFR of 7.5 g/10 min and a decane-soluble component quantity of 0.2 % by weight.

#### Example 28

##### Bulk copolymerization of propylene and ethylene using dimethylmethylen(3-tert-butyl-5-methylcyclopentadienyl) fluorenylzirconium dichloride

[0385] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 25, except that 0.5 NL of hydrogen was added. The quantity of the polymer obtained was 49 g. This polymer had Tm of 120°C, MFR of 65 g/10 min and a decane-soluble component quantity of 0.2 % by weight.



Example 29

Bulk copolymerization of propylene and ethylene using dimethylmethylen(3-tert-butyl-5-methylcyclopentadienyl) (2,7-di-tert-butylfluorenyl)zirconium dichloride

5 [0386] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 25, except that 0.8 mg of the orange solid obtained in Example 5 was used. The quantity of the polymer obtained was 97 g. This polymer had Tm of 126°C, MFR of 2.0 g/10 min and a decane-soluble component quantity of 0.2 % by weight.

10 Example 30

Bulk copolymerization of propylene and ethylene using dimethylmethylen(3-tert-butyl-5-methylcyclopentadienyl) (2,7-di-tert-butylfluorenyl)zirconium dichloride

15 [0387] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 29, except that the charge of ethylene was changed to 4 NL. The quantity of the polymer obtained was 142 g. This polymer had Tm of 116°C, MFR of 4.1 g/10 min and a decane-soluble component quantity of 0.3 % by weight.

20 Example 31

Bulk copolymerization of propylene and ethylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl) fluorenyl zirconium dichloride

25 [0388] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 25, except that 0.7 mg of the reddish brown solid obtained in Example 2 was used. The quantity of the polymer obtained was 89 g. This polymer had Tm of 126°C, MFR of 13.0 g/10 min and a decane-soluble component quantity of 0.2 % by weight.

Example 32

30 Bulk copolymerization of propylene and ethylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl) fluorenyl zirconium dichloride

35 [0389] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 31, except that the charge of ethylene was changed to 3 NL. The quantity of the polymer obtained was 107 g. This polymer had Tm of 122°C, MFR of 18.0 g/10 min and a decane-soluble component quantity of 0.5 % by weight.

Example 33

40 Bulk copolymerization of propylene and ethylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

45 [0390] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 25, except that 1.3 mg of the reddish brown solid obtained in Example 4 was used, and the charge of ethylene was changed to 4 NL. The quantity of the polymer obtained was 297 g. This polymer had Tm of 141°C, MFR of 58 g/10 min and a decane-soluble component quantity of 0.3 % by weight.

Example 34

50 Bulk copolymerization of propylene and ethylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

55 [0391] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 33, except that the charge of ethylene was changed to 5 NL. The quantity of the polymer obtained was 284 g. This polymer had Tm of 137°C, MFR of 97 g/10 min and a decane-soluble component quantity of 0.6 % by weight.

Example 35

Bulk copolymerization of propylene and ethylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

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[0392] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 33, except that the charge of ethylene was changed to 5 NL, and the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 262 g. This polymer had Tm of 137°C, MFR of 115 g/10 min, Mw of 112000, Mn of 62000, Mw/Mn of 1.8 and a decane-soluble component quantity of 0.8 % by weight. As the stereoregularity of the polymer, the mmmm was 95.7 %, the proportion of 2,1-insertion was 0.02 %, and the proportion of 1,3-insertion was 0.18 %.

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Example 36

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Bulk copolymerization of propylene and ethylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0393] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 33, except that the charge of ethylene was changed to 5 NL, and 0.5 NL of hydrogen was added. The quantity of the polymer obtained was 205 g. This polymer had Tm of 131°C, MFR of 310 g/10 and a decane-soluble component quantity of 1.0 % by weight. As the stereoregularity of the polymer, the mmmm was 95.0 %, the proportion of 2,1-insertion was 0.03 %, and the proportion of 1,3-insertion was 0.20 %.

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Example 37

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Pressure solution polymerization of propylene and 1-butene using dimethylmethylenecyclopentadienyl(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0394] A 2000 ml polymerization apparatus thoroughly purged with nitrogen was charged with 900 ml of dry hexane and 30 g of 1-butene at ordinary temperature. Then, the internal temperature of the polymerization apparatus was raised to 70°C, and the apparatus was pressurized to 0.7 MPa with propylene. To the polymerization apparatus, a catalyst solution obtained by adding 0.9 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 1.0 mg (2 µmol) of the reddish orange solid obtained in Example 1 and triisobutylaluminum (1.0 mmol) were added, and polymerization was conducted for 30 minutes with maintaining the internal temperature at 70°C and the propylene pressure at 0.7 MPa. Thereafter, methanol was added to terminate the polymerization. After the pressure was released, a polymer was precipitated from the polymer solution with methanol and dried under vacuum at 130°C for 12 hours. The quantity of the polymer obtained was 9.95 g. This polymer had Tm of 102.7°C and an intrinsic viscosity ( $\eta$ ) of 0.89 dL/g.

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Example 38

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[0395] Polymerization was carried out in the same manner as in Example 37, except that the charge of 1-butene was changed to 60 g. The quantity of the polymer obtained was 7.31 g. This polymer had Tm of 73.6°C and an intrinsic viscosity ( $\eta$ ) of 0.94 dL/g.

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Example 39

[0396] A 2000 ml polymerization apparatus thoroughly purged with nitrogen was charged with 750 ml of dry hexane and 40 g of 1-butene at ordinary temperature. Then, the internal temperature of the polymerization apparatus was raised to 50°C, and the apparatus was pressurized to 0.7 MPa with propylene. To the polymerization apparatus, a catalyst solution obtained by adding 1.35 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 1.5 mg (3 µmol) of the reddish orange solid obtained in Example 1 and triisobutylaluminum (1.0 mmol) were added, and polymerization was conducted for 30 minutes with maintaining the internal temperature at 50°C and the propylene pressure at 0.7 MPa. Thereafter, methanol was added to terminate the polymerization. After the pressure was released, a polymer was precipitated from the polymer solution with methanol and dried under vacuum at 130°C for 12 hours. The quantity of the polymer obtained was 30.0 g. This polymer had Tm of 108.1°C and an intrinsic viscosity ( $\eta$ ) of 2.13 dL/g.

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Example 40

[0397] Polymerization was carried out in the same manner as in Example 39, except that the charge of dry hexane was changed to 700 ml, and the charge of 1-butene was changed to 60 g. The quantity of the polymer obtained was 39.0 g. This polymer had  $T_m$  of 80.0°C and an intrinsic viscosity ( $\eta$ ) of 1.83 dl/g.

Example 41

[0398] A 1000 ml polymerization apparatus thoroughly purged with nitrogen was charged with 830 ml of dry hexane and 70 ml of 1-butene at ordinary temperature. Then, the internal temperature of the polymerization apparatus was raised to 40°C, and the apparatus was pressurized to 0.5 MPa with propylene. To the polymerization apparatus, a catalyst solution obtained by adding 1.35 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 1.5 mg (3  $\mu$ mol) of the reddish orange solid obtained in Example 1 and triisobutylaluminum (1.0 mmol) were added, and polymerization was conducted for 40 minutes with maintaining the internal temperature at 40°C and the propylene pressure at 0.5 MPa. Thereafter, methanol was added to terminate the polymerization. After the pressure was released, a polymer was precipitated from the polymer solution with methanol and dried under vacuum at 130°C for 12 hours. The quantity of the polymer obtained was 25.5 g. This polymer had  $T_m$  of 100.7°C and an intrinsic viscosity ( $\eta$ ) of 3.41 dl/g.

Example 42

[0399] Polymerization was carried out in the same manner as in Example 41, except that the charge of dry hexane was changed to 810 ml, and the charge of 1-butene was changed to 90 ml. The quantity of the polymer obtained was 23.8 g. This polymer had  $T_m$  of 90.6°C and an intrinsic viscosity ( $\eta$ ) of 3.56 dl/g.

Examples 43 - 46

[0400] Films were prepared from the sample polymers obtained in Examples 39 to 42, and properties of the films were measured.

Preparation of film and properties thereof

[0401] On a press plate, an aluminum sheet of 0.1 mm thickness, a polyethylene terephthalate (PET) sheet and an aluminum sheet of 0.1 mm thickness from the center of which a square of 15cm $\times$ 15cm had been cut away were superposed in this order, and on the center (cut portion) of the aluminum sheet, 3.3 g of a sample polymer was placed. Then, a PET sheet, an aluminum plate and a press plate were further superposed in this order.

[0402] The sample polymer interposed between the press plates was placed in a hot press at 200°C and preheated for about 7 minutes. In order to remove bubbles from the sample polymer, an operation of pressure-application (50 kg/cm<sup>2</sup>-G)/pressure-release was repeated several times. Then, the pressure was finally increased to 100 kg/cm<sup>2</sup>-G, and the sample polymer was heated for 2 minutes under pressure. After the pressure was released, the press plates were taken out of the pressing machine, then transferred into a different pressing machine wherein the pressing zone was maintained at 0°C, and cooled under a pressure of 100 kg/cm<sup>2</sup>-G for 4 minutes. After the pressure was released, the sample polymer was taken out. Thus, a film having a uniform thickness of about 0.15 to 0.17 mm was obtained. The properties of the film are set forth in Table 1.

[0403] The properties of the film were measured in the following manner.

## 1. Heat sealing temperature (°C)

[0404] Films were heat sealed by a heat sealer at a given temperature for 1 second under a load of 2 kg/cm<sup>2</sup> to obtain a specimen having a width of 15 mm. The specimen was peeled at a peel rate of 20 mm/min and a peel angle of 180°C. The temperature wherein the peel resistance was 300 g, was taken as a heat sealing temperature.

## 2. Anti-blocking properties (mN/cm)

[0405] Two films superposed upon each other were allowed to adhere under the following conditions; and the anti-blocking properties were measured in accordance with ASTM-D1893.

[0406] The measurement was made after the films were allowed to stand for 24 hours under the adhesion conditions of 50°C and a load of 10 kg.

3.  $\Delta$ Haze (%)

[0407] Using a specimen of 1 mm thickness, the haze was measured by a digital haze meter DH-20D manufactured by Nippon Denshoku Kogyo K.K.

[0408] After a heat treatment of the specimen at 80°C for 3 days, the haze was further measured in the same manner as described above. The difference in haze before and after the heat treatment was taken as  $\Delta$ Haze.

## 4. Static friction coefficient

[0409] The static friction coefficient was measured in accordance with ASTM-D1894.

## 5. Film impact strength (KJ/m)

[0410] The film impact strength was measured at 23°C in accordance with ASTM-D3420.

Table 1

	Ex. 43	Ex. 44	Ex. 45	Ex. 46
Sample polymer in	Polymer obtained Ex. 39	Polymer obtained in Ex. 40	Polymer obtained in Ex. 41	Polymer obtained in Ex. 42
Heat sealing starting temperature (°C)	110	83	100	90
Antiblocking properties (mN/cm)	3	18	1	15
$\Delta$ Haze (%)	0.5	0.2	0.4	0.2
Static friction coefficient	0.9	1.4	1	1.2
Film impact strength (KJ/m)	10.1	5.7	8.7	8.5

## Comparative Example 1

Bulk copolymerization of propylene and ethylene using dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride

[0411] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 27, except that 0.8 mg of dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride was used as metallocene, and the charge of ethylene was changed to 4 NL. The quantity of the polymer obtained was 112 g. This polymer had T<sub>m</sub> of 132°C, MFR of 7 g/10 min, Mw/Mn of 2.9 and a decane-soluble component quantity of 0.7 % by weight. As the stereoregularity of the polymer, the mmmm was 90.4 %, the proportion of 2,1-insertion was 0.79 %, and the proportion of 1,3-insertion was 0.11 %, so that the proportion of 2,1-insertion was high.

## Comparative Example 2

Bulk copolymerization of propylene and ethylene using dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride

[0412] Copolymerization of propylene and ethylene was carried out in the same manner as in Example 27, except that 0.8 mg of dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride was used as metallocene, and the charge of ethylene was changed to 8 NL. The quantity of the polymer obtained was 145 g. This polymer had T<sub>m</sub> of 120°C, MFR of 14 g/10 min, Mw/Mn of 3.4 and a decane-soluble component quantity of 1.1 % by weight. As the stereoregularity of the polymer, the mmmm was 88.8 %, the proportion of 2,1-insertion was 0.69 %, and the proportion of 1,3-insertion was 0.31 %, so that the proportion of 2,1-insertion was high.

Comparative Example 3Properties of random PP prepared using Ziegler-Natta catalyst

- 5 [0413] Properties of commercially available random PP (trade name: F637, available from Grand Polymer Co.) obtained by the use of a magnesium chloride-supported titanium catalyst are as follows. This polymer had T<sub>m</sub> of 142°C, MFR of 6 g/10 min, Mw/Mn of 6.0 and a decane-soluble component quantity of 8.0 % by weight, and the value of Mw/Mn was large. As the stereoregularity of the polymer, the mmmm was 91.1 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

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Comparative Example 4Properties of thermally decomposed product of random PP prepared using Ziegler-Natta catalyst

- 15 [0414] Commercially available random PP (trade name: F637, available from Grand Polymer Co.) obtained by the use of a magnesium chloride-supported titanium catalyst was thermally decomposed under the conditions of 400°C and 100 minutes. Properties of the thus thermally decomposed polymer are as follows. This polymer had T<sub>m</sub> of 140°C, MFR of 1000 g/10 min, Mw/Mn of 2.3 and a decane-soluble component quantity of 22 % by weight, and the decane-soluble component quantity was large. As the stereoregularity of the polymer, the mmmm was 92.0 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

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Example 47

25 Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride

- [0415] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then propylene was bubbled to saturate the apparatus. Thereafter, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 2.35 mg (3.8 μmol) of the red solid obtained in Example 5 was added. With stirring, polymerization was conducted at 25°C for 60 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 0.50 g. This polymer had T<sub>m</sub> of 140°C.

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35 Example 48

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride

- 40 [0416] Polymerization was carried out in the same manner as in Example 47, except that 10.3 mg (16.75 μmol) of the red solid obtained in Example 5 was used, and the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 6.2 g. This polymer had T<sub>m</sub> of 138°C.

45 Example 49

Normal pressure polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

- 50 [0417] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then propylene was bubbled to saturate the apparatus. Thereafter, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 3.27 mg (5.0 μmol) of the red solid obtained in Example 4 was added. With stirring, polymerization was conducted at 25°C for 30 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 0.9 g. This polymer had T<sub>m</sub> of 155°C.

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Example 50

Normal pressure polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0418] Polymerization was carried out in the same manner as in Example 49, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 4.9 g. This polymer had T<sub>m</sub> of 144°C.

Example 51

Normal pressure polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0419] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then propylene was bubbled to saturate the apparatus. Thereafter, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 2.71 mg (5.0 μmol) of the reddish brown solid obtained in Example 2 was added. With stirring, polymerization was conducted at 25°C for 15 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 1.3 g. This polymer had T<sub>m</sub> of 145°C.

Example 52

Normal pressure polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0420] Polymerization was carried out in the same manner as in Example 51, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 3.8 g. This polymer had T<sub>m</sub> of 139°C.

Example 53

Normal pressure polymerization of propylene using dimethylmethylene(3-(1-methyl-1-cyclohexyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl) zirconium dichloride

[0421] Polymerization of propylene was carried out in the same manner as in Example 47, except that 9.61 mg (5 μmol) of the orange solid obtained in Example 7 was used. The quantity of the polymer obtained was 0.3 g. This polymer had T<sub>m</sub> of 147°C.

Example 54

Normal pressure polymerization of propylene using dimethylmethylene(3-(1-methyl-1-cyclohexyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0422] Polymerization was carried out in the same manner as in Example 53, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.2 g. This polymer had T<sub>m</sub> of 134°C.

Example 55

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0423] Polymerization of propylene was carried out in the same manner as in Example 47, except that 1.7 mg (2.5 μmol) of the orange solid obtained in Example 8 was used. The quantity of the polymer obtained was 0.3 g. This polymer had T<sub>m</sub> of 143°C.

Example 56

Normal pressure polymerization of propylene using dimethylmethylen(3-tert-butylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0424] Polymerization was carried out in the same manner as in Example 55, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.4 g. This polymer had Tm of 140°C.

Example 57

Normal pressure polymerization of propylene using dimethylmethylen(3-trimethylsilylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0425] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.7 mg (5 µmol) of the red plate solid obtained in Example 9 was used. The quantity of the polymer obtained was 0.5 g. This polymer had Tm of 137°C.

Example 58

Normal pressure polymerization of propylene using dimethylmethylen(3-trimethylsilylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0426] Polymerization was carried out in the same manner as in Example 57, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 1.1 g. This polymer had Tm of 142°C.

Example 59

Normal pressure polymerization of propylene using dimethylmethylen(3-(1,1-dimethylpropyl)cyclopentadienyl)  
(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0427] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.07 mg (5 µmol) of the red solid obtained in Example 10 was used, and the polymerization time was changed to 45 minutes. The quantity of the polymer obtained was 1.1 g. This polymer had Tm of 150°C.

Example 60

Normal pressure polymerization of propylene using dimethylmethylen(3-(1,1-dimethylpropyl)cyclopentadienyl)  
(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0428] Polymerization was carried out in the same manner as in Example 59, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.74 g. This polymer had Tm of 138°C.

Example 61

Normal pressure polymerization of propylene using dimethylmethylen(3-(1-ethyl-1-methylpropyl)cyclopentadienyl)  
(3,6-di-tert-butylfluorenyl)-zirconium dichloride

[0429] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.15 mg (5 µmol) of the orange solid obtained in Example 11 was used. The quantity of the polymer obtained was 0.13 g. This polymer had Tm of 142°C.

Example 62

Normal pressure polymerization of propylene using dimethylmethylen(3-(1-ethyl-1-methylpropyl)cyclopentadienyl)  
(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0430] Polymerization was carried out in the same manner as in Example 61, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.02 g. This polymer had Tm of 123°C.

Example 63

Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1,3-trimethylbutyl)cyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

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[0431] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.22 mg (5  $\mu$ mol) of the reddish brown solid obtained in Example 12 was used. The quantity of the polymer obtained was 0.62 g. This polymer had Tm of 146°C.

10 Example 64

Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1,3-trimethylbutyl)cyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

15 [0432] Polymerization was carried out in the same manner as in Example 63, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 1.2 g. This polymer had Tm of 136°C.

Example 65

20 Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1-dimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0433] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.14 mg (5  $\mu$ mol) of the red solid obtained in Example 14 was used. The quantity of the polymer obtained was 1.67 g. This polymer had Tm of 149°C.

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Example 66

30 Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1-dimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0434] Polymerization was carried out in the same manner as in Example 65, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 1.2 g. This polymer had Tm of 137°C.

35 Example 67

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl) (2,7-di-tert-butylfluorenyl)zirconium dichloride

40 [0435] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.0 mg (5  $\mu$ mol) of the red solid obtained in Example 15 was used. The quantity of the polymer obtained was 1.27 g. This polymer had Tm of 140°C.

45 Example 68

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl) (2,7-di-tert-butylfluorenyl)zirconium dichloride

50 [0436] Polymerization was carried out in the same manner as in Example 67, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 5.11 g. This polymer had Tm of 137°C.

Example 69

55 Normal pressure polymerization of propylene using diphenylmethylene(3-phenylcyclopentadienyl) (1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0437] Polymerization of propylene was carried out in the same manner as in Example 47, except that 4.27 mg (5  $\mu$ mol) of the reddish orange solid obtained in Example 17 was used. The quantity of the polymer obtained was 0.08



g. This polymer had T<sub>m</sub> of 105°C.

#### Example 70

5 Normal pressure polymerization of propylene using diphenylmethylene(3-trimethylsilylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0438] Polymerization of propylene was carried out in the same manner as in Example 47, except that 4.05 mg (5  
 10 μmol) of the pink powder obtained in Example 18 was used. The quantity of the polymer obtained was 0.18 g. This  
 polymer had T<sub>m</sub> of 139°C.

#### Example 71

15 Normal pressure polymerization of propylene using diphenylmethylene(3-trimethylsilylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0439] Polymerization was carried out in the same manner as in Example 70, except that the polymerization tem-  
 perature was changed to 50°C. The quantity of the polymer obtained was 0.64 g. This polymer had T<sub>m</sub> of 139°C.

#### 20 Example 72

Normal pressure polymerization of propylene using methylphenylmethylene(3-tert-butylcyclopentadienyl) (3,6-di-tert-  
butylfluorenyl)zirconium dichloride

25 [0440] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.32 mg (5  
 μmol) of the orange solid obtained in Example 19 was used, and the polymerization time was changed to 45 minutes.  
 The quantity of the polymer obtained was 1.16 g. This polymer had T<sub>m</sub> of 144°C.

#### 30 Example 73

Normal pressure polymerization of propylene using methylphenylmethylene(3-tert-butylcyclopentadienyl)(3,6-di-tert-  
butylfluorenyl)zirconium dichloride

35 [0441] Polymerization was carried out in the same manner as in Example 72, except that the polymerization tem-  
 perature was changed to 50°C. The quantity of the polymer obtained was 8.65 g. This polymer had T<sub>m</sub> of 144°C.

#### Example 74

40 Normal pressure polymerization of propylene using diethylmethylene(3-tert-butylcyclopentadienyl) (3,6-di-tert-  
butylfluorenyl)zirconium dichloride

[0442] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.14 mg (5  
 45 μmol) of the orange solid obtained in Example 20 was used. The quantity of the polymer obtained was 0.83 g. This  
 polymer had T<sub>m</sub> of 150°C.

#### Example 75

50 Normal pressure polymerization of propylene using diethylmethylene(3-tert-butylcyclopentadienyl)(3,6-di-tert-  
butylfluorenyl)zirconium dichloride

[0443] Polymerization was carried out in the same manner as in Example 74, except that the polymerization tem-  
 perature was changed to 50°C. The quantity of the polymer obtained was 3.15 g. This polymer had T<sub>m</sub> of 143°C.

55

Example 76

Normal pressure polymerization of propylene using cyclohexylidene(3-trimethylsilylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0444] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.3 mg (5  $\mu$ mol) of the orange solid obtained in Example 21 was used. The quantity of the polymer obtained was 0.58 g.  
[0445] This polymer had Tm of 141°C.

Example 77

Normal pressure polymerization of propylene using cyclohexylidene(3-trimethylsilylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0446] Polymerization was carried out in the same manner as in Example 76, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.8 g. This polymer had Tm of 139°C.

Example 78

Normal pressure polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0447] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.13 mg (5  $\mu$ mol) of the orange solid obtained in Example 22 was used. The quantity of the polymer obtained was 0.3 g. This polymer had Tm of 146°C.

Example 79

Normal pressure polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0448] Polymerization was carried out in the same manner as in Example 78, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 3.1 g. This polymer had Tm of 143°C.

Example 80

Normal pressure polymerization of propylene using cyclohexylidene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0449] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.28 mg (5  $\mu$ mol) of the reddish brown solid obtained in Example 23 was used. The quantity of the polymer obtained was 0.37 g. This polymer had Tm of 143°C.

Example 81

Normal pressure polymerization of propylene using cyclohexylidene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0450] Polymerization was carried out in the same manner as in Example 80, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.19 g. This polymer had Tm of 129°C.

Example 82

Normal pressure polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0451] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.67 mg (5  $\mu$ mol) of the red solid obtained in Example 24 was used. The quantity of the polymer obtained was 0.33 g.

Example 83

Normal pressure polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0452] Polymerization was carried out in the same manner as in Example 82, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.37 g.

Example 84

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0453] In a 50 ml two-necked flask thoroughly purged with nitrogen, 2.0 mmol (in terms of aluminum) of silica-supported methylaluminoxane was suspended in 20 ml of heptane. To the suspension, a toluene solution of 1.1 mg (2 μmol) of the reddish brown solid obtained in Example 2 was added, then triisobutylaluminum (1 mmol) was added, and they were stirred for 30 minutes to give a catalyst suspension.

[0454] A 2000 ml autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, and the catalyst suspension was added to perform polymerization at 70°C for 40 minutes under a pressure of 3.0 to 3.5 MPa. Thereafter, methanol was added to terminate the polymerization, and propylene was purged of, to obtain a polymer. The polymer was dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 103 g. This polymer had T<sub>m</sub> of 139°C, MFR of 1.2 g/10 min, Mw of 348000, Mn of 184000, Mw/Mn of 1.9 and a decane-soluble component quantity of 0.5 % by weight.

Example 85

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0455] Polymerization of propylene was carried out in the same manner as in Example 84, except that 2 NL of hydrogen was added. The quantity of the polymer obtained was 55 g. This polymer had T<sub>m</sub> of 141°C, MFR of 1000 g/10 min, Mw of 69000, Mn of 30000, Mw/Mn of 2.3 and a decane-soluble component quantity of 0.8 % by weight. As the stereoregularity of the polymer, the mmmm was 85.8 %, the proportion of 2,1-insertion was 0.08 %, and the proportion of 1,3-insertion was 0.02 %.

Example 86

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0456] Polymerization of propylene was carried out in the same manner as in Example 84, except that 1.3 mg (2 μmol) of the red solid obtained in Example 4 was used. The quantity of the polymer obtained was 49 g. This polymer had T<sub>m</sub> of 155°C, MFR of 1.6 g/10 min, Mw of 357000, Mn of 193000, Mw/Mn of 1.8 and a decane-soluble component quantity of 0.3 % by weight.

Example 87

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0457] Polymerization of propylene was carried out in the same manner as in Example 86, except that 1 NL of hydrogen was added. The quantity of the polymer obtained was 328 g. This polymer had T<sub>m</sub> of 156°C, MFR of 150 g/10 min, Mw of 117000, Mn of 52000, Mw/Mn of 2.3 and a decane-soluble component quantity of 0.1 % by weight. As the stereoregularity of the polymer, the mmmm was 95.6 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

Example 88

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

5 [0458] Polymerization of propylene was carried out in the same manner as in Example 86, except that 1 NL of hydrogen was added, and the polymerization temperature was changed to 60°C. The quantity of the polymer obtained was 252 g. This polymer had Tm of 158°C, MFR of 210 g/10 min, Mw of 97000, Mn of 45000, Mw/Mn of 2.1 and a decane-soluble component quantity of 0.1 % by weight. As the stereoregularity of the polymer, the mmmm was 97.0  
10 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

Example 89

15 Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0459] Polymerization of propylene was carried out in the same manner as in Example 86, except that 0.5 NL of hydrogen was added, and triethylaluminum (1 mmol) was used instead of triisobutylaluminum (1 mmol). The quantity of the polymer obtained was 295 g. This polymer had Tm of 157°C, MFR of 42 g/10 min, Mw of 147000, Mn of 71000,  
20 Mw/Mn of 2.1 and a decane-soluble component quantity of 0.1 % by weight.

Example 90

25 Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride

[0460] Polymerization of propylene was carried out in the same manner as in Example 84, except that 1.2 mg (2 μmol) of the red solid obtained in Example 5 was used. The quantity of the polymer obtained was 41 g. This polymer had Tm of 141°C, MFR of 0.05 g/10 min, Mw of 524000, Mn of 274000, Mw/Mn of 1.9 and a decane-soluble component  
30 quantity of 0.1 % by weight. As the stereoregularity of the polymer, the mmmm was 88.4 %, the proportion of 2,1-insertion was 0.04 %, and the proportion of 1,3-insertion was 0.07 %.

Example 91

35 Bulk polymerization of propylene using dimethylmethylene(3-(1-methyl-1-cyclohexyl)cyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0461] Polymerization of propylene was carried out in the same manner as in Example 84, except that 4.5 mg (7 μmol) of the orange solid obtained in Example 7 was used. The quantity of the polymer obtained was 33 g. This polymer  
40 had Tm of 146°C, MFR of 60 g/10 min, Mw of 115000, Mn of 67000, Mw/Mn of 1.7 and a decane-soluble component quantity of 0.7 % by weight.

Example 92

45 Bulk polymerization of propylene using dimethylmethylene(3-(1-methyl-1-cyclohexyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0462] Polymerization of propylene was carried out in the same manner as in Example 91, except that 1 NL of hydrogen was added. The quantity of the polymer obtained was 24 g. This polymer had Tm of 153°C, MFR of 400 g/  
50 10 min, Mw of 59000, Mn of 30000, Mw/Mn of 2.0 and a decane-soluble component quantity of 1.0 % by weight.

Example 93

55 Bulk polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0463] Polymerization of propylene was carried out in the same manner as in Example 84, except that 1.0 mg (1.4 μmol) of the orange solid obtained in Example 8 was used. The quantity of the polymer obtained was 30 g. This polymer

had Tm of 149°C and MFR of 190 g/10 min.

#### Example 94

5 Bulk polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

10 [0464] Polymerization of propylene was carried out in the same manner as in Example 93, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 183 g. This polymer had Tm of 153°C and MFR of 1000 g/10 min.

#### Example 95

15 Bulk polymerization of propylene using dimethylmethylene(3-trimethylsilylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

20 [0465] Polymerization of propylene was carried out in the same manner as in Example 84, except that 10.68 mg (0.94 µmol) of the red plate solid obtained in Example 9 was used. The quantity of the polymer obtained was 4 g. This polymer had Tm of 136°C.

#### Example 96

25 Bulk polymerization of propylene using dimethylmethylene(3-trimethylsilylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0466] Polymerization of propylene was carried out in the same manner as in Example 95, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 64 g. This polymer had Tm of 143°C.

#### Example 97

30 Bulk polymerization of propylene using dimethylmethylene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

35 [0467] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1 µmol) of the red solid obtained in Example 10 was used. The quantity of the polymer obtained was 54 g. This polymer had Tm of 151°C.

#### Example 98

40 Bulk polymerization of propylene using dimethylmethylene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

45 [0468] Polymerization of propylene was carried out in the same manner as in Example 97, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 91 g. This polymer had Tm of 151°C.

#### Example 99

50 Bulk polymerization of propylene using dimethylmethylene(3-(1-ethyl-1-methylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0469] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1 µmol) of the red solid obtained in Example 11 was used. The quantity of the polymer obtained was 12 g. This polymer had Tm of 147°C.

55

Example 100

Bulk polymerization of propylene using

5 dimethylmethylen(3-(1-ethyl-1-methylpropyl)cyclopentadienyl)(3,6-di-tert-butyl-fluorenyl)zirconium dichloride

[0470] Polymerization of propylene was carried out in the same manner as in Example 99, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 34 g. This polymer had T<sub>m</sub> of 152°C.

10 Example 101

Bulk polymerization of propylene using dimethylmethylen(3-(1,1-dimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

15 [0471] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1 μmol) of the red solid obtained in Example 14 was used. The quantity of the polymer obtained was 29 g. This polymer had T<sub>m</sub> of 147°C and MFR of 350 g/10 min.

Example 102

20

Bulk polymerization of propylene using dimethylmethylen(3-(1,1-dimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

25 [0472] Polymerization of propylene was carried out in the same manner as in Example 101, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 43 g. This polymer had T<sub>m</sub> of 150°C and MFR of 1000 g/10 min.

Example 103

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Bulk polymerization of propylene using dimethylmethylen(3-tert-butylcyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride

35 [0473] Polymerization of propylene was carried out in the same manner as in Example 84, except that 1.3 mg (2 μmol) of the red solid obtained in Example 15 was used. The quantity of the polymer obtained was 42 g. This polymer had T<sub>m</sub> of 137°C and MFR of 1000 g/10 min.

Example 104

40

Bulk polymerization of propylene using dimethylmethylen(3-tert-butylcyclopentadienyl)(2,7-di-tert-butylfluorenyl) zirconium dichloride

[0474] Polymerization of propylene was carried out in the same manner as in Example 103, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 84 g. This polymer had T<sub>m</sub> of 138°C and MFR of 1000 g/10 min.

45

Example 105

Bulk polymerization of propylene using diphenylmethylen(3-trimethylsilylcyclopentadienyl) (1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

50

[0475] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (0.8 μmol) of the pink powder obtained in Example 18 was used. The quantity of the polymer obtained was 6 g. This polymer had T<sub>m</sub> of 141°C.

55

Example 106

Bulk polymerization of propylene using diphenylmethylene(3-trimethylsilylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0476] Polymerization of propylene was carried out in the same manner as in Example 105, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 49 g. This polymer had Tm of 146°C.

Example 107

Bulk polymerization of propylene using methylphenylmethylene(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0477] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (2 µmol) of the orange solid obtained in Example 19 was used. The quantity of the polymer obtained was 87 g. This polymer had Tm of 144°C.

Example 108

Bulk polymerization of propylene using methylphenylmethylene(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride

[0478] Polymerization of propylene was carried out in the same manner as in Example 107, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 148 g. This polymer had Tm of 146°C.

Example 109

Bulk polymerization of propylene using diethylmethylene(3-tert-butylcyclopentadienyl)(3,6-di-tert-butylfluorenyl) zirconium dichloride

[0479] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1 µmol) of the orange solid obtained in Example 20 was used. The quantity of the polymer obtained was 50 g. This polymer had Tm of 149°C.

Example 110

Bulk polymerization of propylene using diethylmethylene (3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride

[0480] Polymerization of propylene was carried out in the same manner as in Example 109, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 89 g. This polymer had Tm of 152°C.

Example 111

Bulk polymerization of propylene using cyclohexylidene(3-trimethylsilylcyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride

[0481] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1 µmol) of the orange solid obtained in Example 21 was used. The quantity of the polymer obtained was 20 g. This polymer had Tm of 139°C.

Example 112

Bulk polymerization of propylene using cyclohexylidene(3-trimethylsilylcyclopentadienyl)(3,6-di-tert-butylfluorenyl) zirconium dichloride

[0482] Polymerization of propylene was carried out in the same manner as in Example 111, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 43 g. This polymer had Tm of 141°C, MFR of 1000 g/

10 min and a decane-soluble component quantity of 0.5 % by weight.

Example 113

5 Bulk polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(3,6-di-tert-butylfluorenyl) zirconium dichloride

10 [0483] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1  $\mu$ mol) of the orange solid obtained in Example 17 was used. The quantity of the polymer obtained was 49 g. This polymer had Tm of 149°C and MFR of 190 g/10 min.

Example 114

15 Bulk polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride

20 [0484] Polymerization of propylene was carried out in the same manner as in Example 113, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 118 g. This polymer had Tm of 151°C and MFR of 1000 g/10 min.

Example 115

25 Bulk polymerization of propylene using cyclohexylidene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0485] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1  $\mu$ mol) of the reddish brown solid obtained in Example 23 was used. The quantity of the polymer obtained was 3 g. This polymer had Tm of 141°C.

30 Example 116

Bulk polymerization of propylene using cyclohexylidene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

35 [0486] Polymerization of propylene was carried out in the same manner as in Example 115, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 47 g. This polymer had Tm of 150°C.

Example 117

40 Bulk polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

45 [0487] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (0.9  $\mu$ mol) of the red solid obtained in Example 24 was used. The quantity of the polymer obtained was 3 g. This polymer had Tm of 143°C.

Example 118

50 Bulk polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl) (1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0488] Polymerization of propylene was carried out in the same manner as in Example 117, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 87 g. This polymer had Tm of 152°C.

55



Comparative Example 5Bulk polymerization of propylene using dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride

- 5 [0489] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.8 mg of dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride was used as metallocene. The quantity of the polymer obtained was 150 g. This polymer had T<sub>m</sub> of 145°C, MFR of 16 g/10 min, Mw/Mn of 2.1 and a decane-soluble component quantity of 0.4 % by weight. As the stereoregularity of the polymer, the mmmm was 93.0 %, the proportion of 2,1-insertion was 0.75 %, the proportion of 1,3-insertion was 0.06 %, and the proportion of the 2,1-insertion was high.

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Comparative Example 6Bulk polymerization of propylene using dimethylsilylenebis(2-methyl-4-phenylindenyl)zirconium dichloride

- 15 [0490] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.7 mg of dimethylsilylenebis(2-methyl-4-phenylindenyl)zirconium dichloride was used as metallocene. The quantity of the polymer obtained was 163 g. This polymer had T<sub>m</sub> of 150°C, MFR of 1 g/10 min, Mw/Mn of 2.5 and a decane-soluble component quantity of 0.6 % by weight. As the stereoregularity of the polymer, the mmmm was 95.9 %, the proportion of 2,1-insertion was 0.80 %, the proportion of 1,3-insertion was 0.05 %, and the proportion of the 2,1-insertion was high.

20

Comparative Example 7Properties of homo-PP prepared using Ziegler-Natta catalyst

- 25 [0491] Properties of commercially available homo-PP (trade name: J700, available from Grand Polymer Co.) obtained by the use of a magnesium chloride-supported titanium catalyst are as follows. This polymer had T<sub>m</sub> of 161°C, MFR of 11 g/10 min, Mw/Mn of 5.2 and a decane-soluble component quantity of 2.0 % by weight, and the value of Mw/Mn was large. As the stereoregularity of the polymer, the mmmm was 95.0 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

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Comparative Example 8Properties of thermally decomposed product of homo-PP prepared using Ziegler-Natta catalyst

- 35 [0492] Commercially available homo-PP (trade name: J700, available from Grand Polymer Co.) obtained by the use of a magnesium chloride-supported titanium catalyst was thermally decomposed under the conditions of 400°C and 100 minutes. Properties of the thus thermally decomposed polymer are as follows. This polymer had T<sub>m</sub> of 160°C, MFR of 1000 g/10 min, Mw/Mn of 2.3 and a decane-soluble component quantity of 15 % by weight, and the decane-soluble component quantity was large. As the stereoregularity of the polymer, the mmmm was 94.9 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

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Example 119Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

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- [0493] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then the apparatus was purged with propylene. Then, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 3.1 mg (5 μmol) of the orange solid obtained in Example 3 was added. With stirring, polymerization was conducted at 25°C for 30 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 0.7 g. This polymer had T<sub>m</sub> of 155°C.

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Example 120

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0494] Polymerization was carried out in the same manner as in Example 119, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 1.6 g. This polymer had T<sub>m</sub> of 144°C.

Example 121

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0495] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then propylene was bubbled to saturate the apparatus. Thereafter, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 2.51 mg (5.0 μmol) of the reddish orange solid obtained in Example 1 was added. With stirring, polymerization was conducted at 25°C for 10 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 0.9 g. This polymer had T<sub>m</sub> of 146°C.

Example 122

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0496] Polymerization was carried out in the same manner as in Example 121, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.9 g. This polymer had T<sub>m</sub> of 134°C.

Example 123

Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0497] In a 50 ml two-necked flask thoroughly purged with nitrogen, 2.0 mmol (in terms of aluminum) of silica-supported methylaluminoxane was suspended in 20 ml of heptane. To the suspension, a toluene solution of 1.0 mg (2 μmol) of the reddish orange solid obtained in Example 1 was added, then triisobutylaluminum (1 mmol) was added, and they were stirred for 30 minutes to give a catalyst suspension.

[0498] A 2000 ml autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, and the catalyst suspension was added to perform polymerization at 70°C for 40 minutes under a pressure of 3.0 to 3.5 MPa. Thereafter, methanol was added to terminate the polymerization, and propylene was purged of, to obtain a polymer. The polymer was dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 102 g. This polymer had T<sub>m</sub> of 139°C, MFR of 0.7 g/10 min, Mw of 406000, Mn of 197000, Mw/Mn of 2.1 and a decane-soluble component quantity of 0.1 % by weight.

Example 124

Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0499] Polymerization of propylene was carried out in the same manner as in Example 123, except that 1 NL of hydrogen was added. The quantity of the polymer obtained was 69 g. This polymer had T<sub>m</sub> of 142°C, MFR of 22 g/10 min, Mw of 185000, Mn of 80000, Mw/Mn of 2.3 and a decane-soluble component quantity of 0.4 % by weight. As the stereoregularity of the polymer, the mmmm was 86.9 %, the proportion of 2,1-insertion was 0.02 %, and the proportion of 1,3-insertion was 0.05 %.

Example 125

Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0500] Polymerization of propylene was carried out in the same manner as in Example 123, except that 1.1 mg (1.8  $\mu$ mol) of the orange solid obtained in Example 3 was used. The quantity of the polymer obtained was 90 g. This polymer had Tm of 154 °C, MFR of 1.8 g/10 min, Mw of 321000, Mn of 154000, Mw/Mn of 2.3 and a decane-soluble component quantity of 0.1 % by weight.

Example 126

Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0501] Polymerization of propylene was carried out in the same manner as in Example 125, except that 1 NL of hydrogen was added. The quantity of the polymer obtained was 135 g. This polymer had Tm of 156°C, MFR of 350 g/10 min, Mw of 82000, Mn of 37000, Mw/Mn of 2.2 and a decane-soluble component quantity of 0.2 % by weight. As the stereoregularity of the polymer, the mmmm was 94.8 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

Comparative Example 9

Synthesis of dimethylmethylene (3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride containing isomer

(1) Synthesis of 2,6,6-trimethylfulvene

[0502] To 130 ml of dehydrated methanol, 22.6 g (283 mmol) of methylcyclopentadiene and 8.50 ml (116 mmol) of acetone were added, then 14.5 ml (174 mmol) of pyrrolidine was dropwise added at 0°C, and the mixture was reacted at room temperature for one night. Then, 10 ml (180 mmol) of acetic acid was added at 0°C. The mixture was diluted with ether and water and then subjected to extraction. Then, the organic phase was separated, washed with water and dried over anhydrous magnesium sulfate to obtain 12.9 g of a brown liquid. The analyzed values are given below.

[0503] <sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS, main peak):  $\delta$ 6.49 (d, 1H), 6.32 (d, 1H), 6.17 (s, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.06 (s, 3H)

(2) Synthesis of 1-tert-butyl-3-methylcyclopentadiene

[0504] In a 300 ml flask purged with nitrogen, 2.86 g (23.8 mmol) of trimethylfulvene synthesized in the above step (1) and 80 ml of dry ether were placed. Then, 17 ml (23.8 mmol) of a methylolithium/ether solution (concentration: 1.4 mol/liter) was dropwise added at -78°C, and the mixture was reacted at room temperature for 2 days. Then, 20 ml of an ammonium chloride saturated aqueous solution was added, and the organic phase was separated, washed with water, washed with a sodium chloride saturated aqueous solution and dried over anhydrous magnesium sulfate. Thereafter, the solvent was distilled off, and the residue was purified by column chromatography (silica gel, developing solvent: hexane) to obtain 2.04 g of a brown liquid. The analyzed values are given below.

[0505] <sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS, main peak):  $\delta$ 6.31+6.13+5.94+5.87 (s+s+t+d, 2H), 3.04+2.95 (s+s, 2H), 2.17+2.09 (s+s, 3H), 1.27 (d, 9H)

[0506] Peaks derived from proton of an isomer were observed in the vicinity of  $\delta$ 5.5 and 5.1. From the integral value of proton, the ratio of the presence between the main product and the by-product proved to be about 8:1.

(3) Synthesis of dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0507] Dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride was synthesized in the same manner as in the steps (3) and (4) of Example 1, except that 1-tert-butyl-3-methylcyclopentadiene containing an isomer obtained in the step (2) was used.

[0508] Peaks derived from proton of an isomer were observed in the vicinity of  $\delta$ 7.4 and 6.1. From the integral value of proton, the ratio of the presence between the main product and the by-product proved to be about 8:1.

Comparative Example 10Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride containing isomer

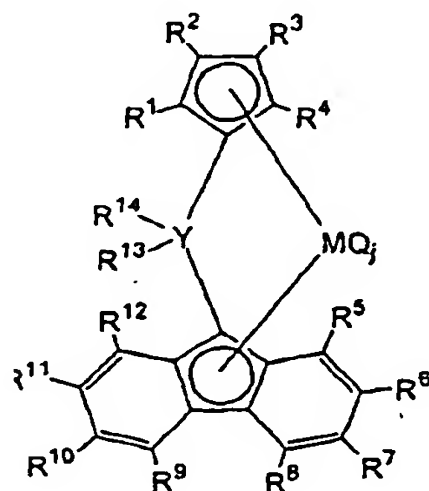
[0509] Polymerization of propylene was carried out in the same manner as in Example 84, except that dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride containing an isomer obtained in Comparative Example 9 was used. The quantity of the polymer obtained was 89 g. This polymer had Tm of 138°C, Mw of 394000 and Mn of 197000. The decane-soluble component quantity was 2.5 % by weight and was large.

Comparative Example 11Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride containing isomer

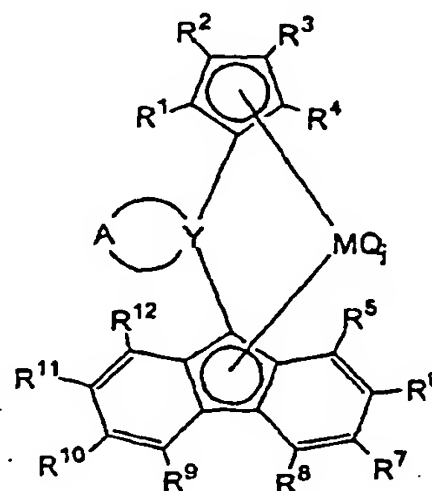
[0510] Polymerization of propylene was carried out in the same manner as in Comparative Example 10, except that 2 NL of hydrogen was added. The quantity of the polymer obtained was 54 g. This polymer had Tm of 140°C, MFR of 130 g/10 min, Mw of 135000 and Mn of 34000. The decane-soluble component quantity was 4.5 % by weight and was large.

Claims

1. A metallocene compound represented by the following formula (1) or (2):



... (1)



... (2)

wherein R<sup>3</sup> is selected from a hydrocarbon group and a silicon-containing hydrocarbon group; R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup> and R<sup>14</sup> may be the same or different and are each selected from a hydrogen atom, a hydrocarbon group and a silicon-containing hydrocarbon group; of the groups indicated by R<sup>1</sup> to R<sup>12</sup>, neighboring groups may be bonded to form a ring; In case of the formula (1), a group selected from R<sup>1</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>12</sup> may be bonded to R<sup>13</sup> or R<sup>14</sup> to form a ring; A is a divalent hydrocarbon group of 2 to 20 carbon atoms which may contain an unsaturated bond and/or an aromatic ring; A may contain two or more cyclic structures including a ring formed by A in cooperation with Y; Y is a carbon atom or a silicon atom; M is a metal selected from Group 4 of the periodic table; j is an integer of 1 to 4; Q is selected from a halogen atom, a hydrocarbon group, an anionic ligand and a neutral ligand capable of coordination by a lone pair; and when j is 2 or greater, each Q may be the same or different.

2. A metallocene compound represented by the following formula (1a) or (2a):